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SOME ASPECTS OF MATHEMATICAL AND CHEMICAL MODELING
OF COMPLEX CHEMICAL PROCESSES

I. Nemes, L. Botar, E. Danoczy,
T. Vidoczy and D. Gal



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14. Abstract Some theoretical questions involved in mathematical modeling of the kinetics of complex chemical processes are discussed. The analysis is carried out for the homogeneous oxidation of ethyl- benzene in the liquid phase. Particular attention is given to the determination of the general charac- teristics of chemical systems from an analysis of mathematical models developed on the basis of linear algebra.			
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Some Aspects of Mathematical and Chemical Modeling
of Complex Chemical Processes

I. Nemes, L. Botar, E. Danoczy,
T. Vidoczy, and D. Gal

The Central Scientific Research Institute
of Chemistry, Budapest

The paper studies theoretical matters in the mathematical modeling of the kinetics of arbitrary complex chemical processes, using the example of homogeneous liquid-phase oxidation of ethylbenzene.

It is known that mathematical models of chemical transformations are usually specified in the following forms: /427*

1. Algebraic forms; these forms use the methods of linear algebra and certain characteristics of the chemical system are given in terms of the characteristics of a n-dimensional vector (linear) space [1], [2], [3], [4].

2. A set of differential equations; this form is the classical for a mathematical model in chemical kinetics.

3. Models of random processes, in which models the transpiration of a particular elementary event is evaluated from the standpoint of the probability of this process during a particular interval of time [5].

The model used most often in chemical kinetics and the most convenient in form is that given by a set of differential equations. In this case, the functional relations obtained after integration can be compared with those observed in prac-

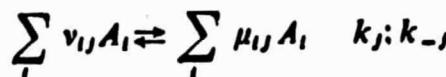
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tice. These relations can also be used to solve most easily the problem of refining the estimates for necessary kinetic parameters, once their provisional estimates are known, or to make a determination of these parameters by means of statistical criteria.

The mathematical models created with the help of linear algebra seem at first glance less useful, although a study of these can clarify important common features of chemical systems. It is in fact the clarification of these common characteristics that is the aim of our theoretical investigation: by detailed analysis of mathematical models of chemical kinetics, elaborated with the help of linear algebra methods.

By a complex chemical system we understand a set of simple reactions. In the chemical literature, as is known, a j -th ($j = 1, 2, \dots, m$) simple reaction of a given complex process that takes place in the space of chemical particles $A_1, A_2, \dots, A_1, \dots, A_N$, is understood to be the chemical reaction:

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where v_{ij} and μ_{ij} are stoichiometric coefficients, with:

a) $v_{ij}, \mu_{ij} = 0, 1, 2$ or 3

b) $\sum_i v_{ij}, \sum_i \mu_{ij} \leq 3$

they uniquely determine the rate (the rate function) of the j -th elementary reaction in the form:

$$W_j = k_j \prod_i [A_i]^{-v_{ij}} - k_j \prod_i [A_i]^{\mu_{ij}}$$

(here $[A_i] = F_i(t)$ is the temporal concentration of the i -th particle).

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Let us introduce a new concept, that of the "half-reaction": hereafter we shall call the symbols:

$$\sum_i v_{ij} A_i \text{ and } \sum_i \mu_{ij} A_i$$

figuring in the chemical equation of the j -th elementary reaction of a complex system, as well as the symbols:

$$/\!/ [A_i]^{''''} \text{ and } /\!/ [A_i]^{''''}$$

figuring in the expression for the rate of the j -th elementary reaction the "half-reactions".

In this case we can write the j -th elementary reaction in the form:

$$F_j \rightleftharpoons F_{j+1}$$

Similarly, the rate of the j -th elementary reaction will be:

$$W_j = k_j F_j - k_{j-1} F_{j-1}$$

Hereafter we shall describe complex chemical systems by the following principal matrices:

1. The stoichiometric matrix of the system. The matrix A , as is known, is constructed as follows: the j -th element of the i -th column will be $-v_{ij}$ or μ_{ij} , depending on whether the chemical particle A_i participates on the "right" or "left" side of the chemical equation of the j -th elementary reaction.

2. The kinetic matrix of the system (k), defined in the following manner: the j -th element of the l -th column will be the constant rate of the half-reaction F_j (we shall also take into account the sign of this element). This latter term figures in the expression for the rate of the j -th elementary reaction

(here $l = 1, 2, \dots, f$ and f is the number of half-reactions in the reaction system).

We shall further introduce the concept:

1. The maximum number of linearly-independent elementary reactions of a complex reaction system shall be known as the stoichiometric dimension (D_{st}) of the system. If $D_{st} = m$, the system is stoichiometrically independent; if $D_{st} < m$, the system is known as stoichiometrically dependent.

2. The maximum number of linearly independent rate functions¹ (rates) of the reaction system shall be called the kinetic dimension (D_K) of the system. If $D_K = m$, the system is independent in the kinetic sense; if $D_K < m$, the system is known as kinetically dependent.

On the basis of algebraic models it is easy to prove the following [2], [3], [6], [7]:

1. The rank of the matrix A equals the stoichiometric dimension of the chemical system:

$$r(A) = D_{st}$$

2. The maximum number of linearly-independent differential equations written for the given complex system in the form:

$$K = AW, \dot{K} = ([\dot{A}_1], \dots, [\dot{A}_N])^T$$

is exactly equal to D_{st} and, as is known, the number of linearly dependent material-balance equations of type:

¹The rates of simple reactions of a chemical system are linearly independent if the equality $\sum c_j w_j = 0$ is satisfied then and only when all c_j are identically equal to zero.

$$\sum_i x_{ii} [A_i] = 0$$

is exactly equal to $N-r(\dot{A})$ in kinetically-independent systems.

We have been able to prove that the number of independent material-balance equations does not differ from $N-r(\dot{A})$ for kinetically-independent systems either.

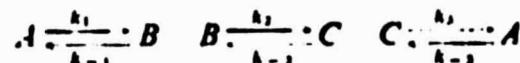
3. The kinetic dimension of an arbitrary reaction system corresponds to the rank of the kinetic matrix k , i.e.

$$r(k) = D_k$$

4. In an arbitrary reaction system the stoichiometric dimension cannot be larger than the kinetic dimension, i.e.

$$D_s \leq D_k$$

An analysis of the linear dependence or independence of the rate of reaction systems enables an identification of useful functional relationships and provides new "rate-balance equations". Let us assume, e.g., that our reaction system is:



Since the kinetic dimension of this system is $D_k = 2$, the rates of the system are linearly-dependent. If the experimental conditions allow a measurement of the rates W_1, W_2, W_3 (for example by the method of kinetic isotopes), a direct determination of the rate constant ratio seems possible from the set of equations:

$$\frac{k_3}{k_1} W_1(t_1) + \frac{k_3}{k_{-2}} W_2(t_1) = -W_3(t_1) \quad \frac{k_{-3}}{k_1} W_1(t_2) + \frac{k_3}{k_{-2}} W_2(t_2) = -W_3(t_2)$$

where

$W_1(t_1), W_2(t_1), W_3(t_1)$ is the rate at moment t_1 ,

$W_1(t_2), W_2(t_2), W_3(t_2)$ is the rate at moment t_2 .

In order to determine the kinetic dimensions of a chemical system we have developed a simple and elegant method on the basis of graph theory, as a consequence of which the complicated task of determining the rank of the matrix becomes unnecessary. /430

The chief aim of our research on the oxidation of ethylbenzene is to clarify the mechanism of oxidation on the basis of kinetic measurements. The heart of the customary classical method of determination of the mechanism consists in an "approximation from the bottom", i.e. a consecutive approximation to an agreeable mechanism¹ of the complex chemical process. Our method starts with a new concept, that of system theory. To each complex chemical transformation we ascribe a so-called "possible mechanism" of the process, comprised of those elementary reactions in the given space of reacting particles that:

- a) are thermodynamically possible and necessary in the chemical respect,
- b) are not excluded by study of similar chemical systems.

In the most general case, regardless of the type of investigated process, we always have at our disposal a certain initial system of information. This information can always be used as the basis for a choice of a certain minimum number of reactions from the elementary reactions of the possible mechanism that will necessarily occur from the standpoint of the initial system of information. We shall call this system the null mechanism.

¹By agreeable mechanism we understand a system of elementary reactions with set of differential kinetic equations within the limits of the given experimental errors that is most close to the experimental curves and at the same time contains the minimum necessary number of simple reactions.

Let us assume that:

An agreeable mechanism of the studied complex process is included in the possible mechanism and includes the null mechanism of the complex process.

Each experimental datum can either increase the number of elementary reactions of the null mechanism or reduce the number of reactions of the possible mechanism (exclude certain reactions from it).

This two-way approximation - "from the bottom and from the top" - leads to a determination of an agreeable mechanism of a complex process at the particular stage of the experiment.

Determination of an agreeable mechanism is a special form of chemical modeling.

After putting together a possible mechanism for a complex chemical process, the chief task consists in the actual chemical modeling of the process.

Modeling of this type basically consists in a planning and organization of such experiments that can provide a maximum amount of experimental data for the formulation of an agreeable mechanism of the complex process.

The aim of the actual chemical modeling of the complex process of ethylbenzene oxidation is the confirmation, with a certain large degree of probability, of the elementary processes that take part in the complex transformation of substances, and quantitative interpretation of the kinetic data on the basis of a well-chosen mechanism.

To achieve this goal, our scheduled experiments are different

in nature, qualitatively different. This difference can be described by an analogy taken from biology: a) a series of experiments "in vivo"; b) a series of experiments "in vitro".

Experiments "in vivo". This group of experiments is based on a knowledge of the probable "network" of a complex process. By "network" we understand the sequence of formation of intermediate and end products. The task consists in proving the correctness of the proposed "network" and determining its internal links in the form of quantitative relations.

In the case of ethylbenzene oxidation, the possible "network" was formed on the basis of our own experiment and the literature data [8]-[18].

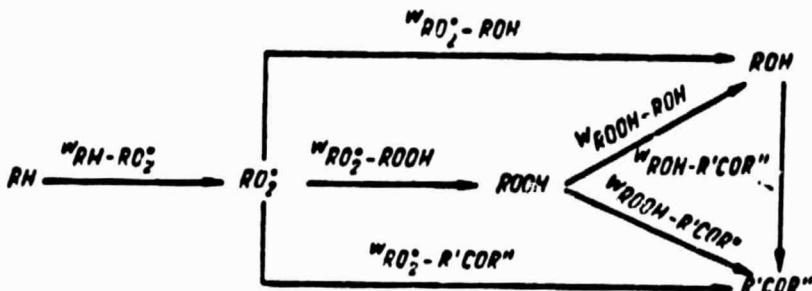


Fig. 1

The anticipated transitions shown by arrows correspond to certain subsystems of the possible mechanism as determined in the second part - oxidation of ethylbenzene. The time dependence of the rates of these subsystems reflects the action of conversion on the relative role of the elementary processes that take part in the given subsystems.

The rates and their time dependences are determined by means of the isotope method.

On the basis of our experimental data [19]-[22] we computed

that the majority of intermediate products formed during the course of the reaction are more reactive in a reaction with chain-lengthening radicals, than the original hydrocarbon. All of this indicates that, as conversion increases, those reactions in which the intermediate products are used up become dominant.

Experiments "in vitro". On the results of "in vivo" experiments, a modeling of the individual subsystems was planned. Experiments were organized: the alcohol-ketone, hydroperoxide-alcohol, hydroperoxide-ketone transition and the radical-alcohol and radical-ketone transitions. To understand these transitions it is necessary to study the independent chemical systems by various experimental methods.

It follows from our results that the alcohol-ketone transition takes place under radical-initiated oxidation of alcohol. Further, the results of experiments using O^{18} [19] show that, as the alcohol concentration increases, the nature of the radicals advancing the chain alters, i.e. there is apparently a gradual change in the actual method of the complex oxidation process.

Submitted Sept. 1973.

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